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CATALYST FOR THE SYNTHESIS OF AMMONIA FROM HYDROGEN AND NITROGEN

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The present invention relates to a catalyst for the synthesis of ammonia from hydrogen and nitrogen.

Description of Related Art

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The ammonia synthesis catalyst play an important role in the manufacture of ammonia. It effects both the economics and operating conditions of ammonia plants.

Industrial catalysts for ammonia synthesis must satisfy a number of requirements: high catalyst activity at the lowest possible reaction temperatures in order to take advantage of the favourable thermodynamic equilibrium at low temperatures, good resistance to poisoning by oxygen-, chlorine- and sulphur -containing compounds, long life and high mechanical strength.

In order to save energy the synthesis pressure has been steadily reduced from 250-350 bar to 80-150 bar during the last 30 years due to optimised operation of the synthesis loop made possible by new technology, especially for fabrication of the converter. Improvements in the front end has drastically reduced the content of catalyst poisons (oxygen- , sulphur- and chlorine-containing compounds) in the gas inlet to the converter. However, the drop in synthesis pressure necessitates a three- to four-fold increase in the catalyst volume. The demands upon the catalyst quality has also increased. Apparently small improvements in the catalyst activity may lead to major improvements of the operation of a modern ammonia synthesis loop.

The ammonia synthesis catalyst precursor, the unreduced catalyst, is manufactured by melting iron oxides, mainly magnetite, and oxides or carbonates of Al, K, Ca and Mg, the so-called promoters. The melting is performed in electrical furnaces at a temperature of above 1600 °C. The ratio Fe^{2+}/Fe^{3+} in the melt is normally in the range 0.5-0.75. The melt is then poured into metal trays where it solidifies and cools. The

solid precursor is then broken up, crushed and sieved to obtain the required grain size.

The precursor is reduced to active iron catalyst "in situ" in the ammonia synthesis converter or used to manufacture the prereduced catalyst by a complete reduction under optimised conditions in a prereduction reactor. This material is pyroforic, but after a skin oxidation of the active surface with oxygen, it can be handled safely in air at ambient temperatures.

The promoters mentioned above, containing Al, K,Ca and Mg, are essential for the formation of a large surface of iron in the reduced catalyst and for the kinetics of ammonia formation.
Since the development of the catalyst started, about 90 years ago, the concentration of these promoters have been optimised to obtain maximum activity and to meet the additional requirement mentioned above. Further improvements seem only possible by adding new promoters, or new combination of promoters.

Cobalt oxide has been used as such a new promoter.
From US patent 3839229 it is known an ammonia synthesis catalyst where cobalt oxide is used as a promoter. The catalyst consists essentially of a solid solution of iron oxide and cobalt oxide and said cobalt oxide is present in an amount of 5 to 10 percent by weight expressed as cobalt. In the catalyst there is further included a promoter selected from the group consisting of alumina, silica, zirconia, magnesia, lime (CaO),potassium oxide and rare earth metal oxides.

Another possible promoter is titanium oxide. Only few catalysts using this promoter have been previously described. S.A. Abdukadyrova et al. have in "Tr.Mosk.Khim.-Tekhnol.Inst. (1970),No.2,122-5",
described that titanium oxide improves the thermal resistance but reduces the activity.

Titanium oxide used as a structural promoter is described by M. E. Dry et al in "Journal of Catalysis", 6, page:194-199, 1966. Titanium oxide is not so effective as aluminium oxide with regard to surface area. This area and the volume of

chemisorbed CO normally increase with promoter content, but in contrast to the other promoters (Al_2O_3, MgO, CaO) TiO_2 had a maximum in the volume of chemisorbed CO at about 0.5 g atom cation per 100 g atom Fe.

a BRIEF SUMMARY OF THE INVENTION

The main object of the present invention was to develop a catalyst for ammonia synthesis with improved activity.

Higher activity could be utilized in two ways: High reaction rate at high ammonia concentrations or higher activity at low temperatures.
The catalyst activity may be expressed as a rate constant in a rate equation for the synthesis reaction. The rate is a function of temperature, pressure and the composition of the gas, and decreases rapidly with increasing ammonia concentrations. Thus a large fraction of the catalyst volume in a synthesis converter will have ammonia concentration approaching the exit concentration. Hence, to improve the efficiency, increasing the reaction rate at high ammonia concentration is of perticular interest.
As the equilibrium temperature decreases with increasing ammonia concentration, searching higher conversion by increasing the reaction rate at high ammonia concentration also means searching a catalyst with higher activity at low temperature.

The inventors have manufactured a lot of samples of iron oxide based catalysts with various promoters in various concentrations to improve the catalyst activity. In addition to the conventional promoters mentioned above, new promoters have been tested, in particular cobalt- and titanium oxide.

The inventors found that the reaction rate at high ammonia concentration increased with 10-20% when both cobalt- and titanium oxide were used as promoters together with the conventional promoters.

The most preferred catalyst was achieved when the concentration of cobalt was between 0.1% and 3.0 % by weight of metal and when the concentration of titanium was between 0.1 % and 1.0 % by weight of metal.

The atomic ratio Fe^{2+}/Fe^{3+} was between 0.5-0.65.

The present invention will thus in its widest scope comprise a catalyst for the synthesis of ammonia from hydrogen and nitrogen consisting of iron oxides and promoters where the promoters comprise oxides of both cobalt and titanium in addition to Al, K, Ca and Mg oxides.

The invention will be further explained in the example.

a DETAILED DESCRIPTION OF THE INVENTION

Example:

Samples were made by mixing iron ore, mainly magnetite, Fe_3O_4, with promoters. These mixtures were then melted in a ceramic crucible in a laboratory furnace. The temperature was kept at about 1600 °C. The ratio of Fe^{2+}/Fe^{3+} was adjusted to within 0.5 to 0.65 by adding Fe-metal to the melt.

The melt was then poured into an iron crucible and cooled.

The concentration of the promoters in the samples varied as shown in table I:

Table I:

K	0.4 - 0.5
Ca	1.6 - 1.8
Mg	0.3 - 0.5
Al	1.5 - 1.8
Co	0.10- 3.00
Ti	0.14- 0.95

The balance being iron oxides with natural impurities. The cooled samples were crushed and sieved to 0.4 - 0.63 mm particles for testing in a microreactor.

The samples, (10 g each), were tested together with the reference sample in a microreactor. The reference sample was a conventional catalyst with no cobalt- or titanium oxide added.

The samples were reduced in a flow of H_2 and N_2 in the ratio 3/1 at a space velocity of 33000 1 /h. The increase in temperature was 3°C/h from 250°C to 520° C and 520° C was kept for 24 hours to ensure complete reduction.

The samples were then tested at a pressure of 50 bar, space velocity in the range 8000 to 50000 1/h, and temperatures in the range 350°C to 420° C. The inlet gas was H_2/N_2=3/1 with an ammonia concentration of 1.0 to 1.2 % (vol.). Exit ammonia concentration was in the range 4 to 9 % (vol.).

The data obtained during a period of about 100 hours and after an initial stabilisation of 24 hours or more, were used to calculate parameters in a kinetic model for the reaction. The model was then further used for calculating the relative activity and relative reaction rate at higher ammonia concentration than used in the test.

The following table II shows the concentration of cobalt and titanium in the various samples, average relative catalyst activities and predicted relative reaction rate at higher ammonia concentration (20% NH_3, 420°C) calculated by the kinetic model.

Table II:

Sample	Co w %	Ti w %	Average Relative Catalyst Activity at 350°C	Relative Reaction Rate (20% NH_3 and 420°C)	Average Relative Catalyst Activity at 420°C
1 (reference)	0	0.14 (impurity)	1.0	1.0	1.0
2	1.38	0.14 "	1.0	1.06	1.06
3	2.94	0.14 "	1.04	1.08	1.13
4	0.1	0.83	0.91	0.86	0.91
5	0.1	0.4	0.71	0.97	0.93
6	0.1	0.91	1.04	0.91	1.02
7	1.24	0.41	1.08	1.13	1.18
8	0.35	0.38	1.04	1.22	1.13
9	0.56	0.54	1.12	1.22	1.17

Table II shows that the relative reaction rate was highest at high concentration of ammonia (20%) when both cobalt oxide and titanium oxide were added as promoters (compare sample 7-9 with sample 1).
Furthermore, the table II shows that by adding either cobalt oxide or titanium oxide alone, together with the other conventional promoters, a lower relative reaction rate at high concentration of ammonia was obtained (compare samples 2-3 and 4-6 with sample 1).
Furthermore, table II shows that the activity was increased at temperatures down to 350°C when both cobalt- and titanium oxide were added as extra promoters (see sample 7-9).
The example also shows that the activity was increased both at low and high reaction temperature when both cobalt- and titanium oxide were added as promoters.